sition of hydrocarbons. Examples are the manufacture of carbon black (Chap. 5) and acetylene (Chap. 7).

In Europe, *formic acid* is made by the oxidation of formamide. "All formic acid produced in the United States is produced as a by-product of the liquid phase oxidation of *n*-butane to acetic acid."[27] The by-product source is expected to dry up in the future, and the most promising route to replace it is through carbonylation of methanol.

Caprolactam, adipic acid, and hexamethylene diamine[28] are all made from cyclohexane. Almost all high-purity cyclohexane is obtained by hydrogenating benzene, although some for solvent use is obtained by careful distillation of selected petroleum fractions.

Several oxidative routes are available to change cyclohexane to cyclohexanone, cyclohexanol, and ultimately to adipic acid or caprolactam. If phenol is hydrogenated, cyclohexanone can be obtained directly; this will react with hydroxylamine to give cyclohexanone oxime which converts to caprolactam on acid rearrangement (Chap. 35). Cyclohexane can also be converted to adipic acid, then adiponitrile, which can be converted to hexamethylenediamine. Adipic acid and hexamethylenediamine are used to form nylon 6,6. This route to HMDA is competitive with alternative routes through butene.

Acetaldehyde has a brisk sale as a precursor of acetic acid, 1,3-butylene glycol, glyoxal, pentaerythritol, peracetic acid, and pyridines. The demand in 1981 was 409×10^6 kg. There are several competing processes. (1) The older process by the hydration of acetylene is no longer significant. (2) The Wacker process developed by Hoechst[29] starts with ethylene and oxidizes it directly with air or 99% oxygen (Fig. 38.9). The catalyst is palladium chloride with a copper chloride promoter. The ethylene gas is bubbled, at atmospheric pressure, through the solution at its boiling point. The heat of reaction is removed by boiling of the water. Unreacted gas is recycled following condensation of the aldehyde and water, which are then separated by distillation. (3) Passing ethyl alcohol over a copper or silver gauze catalyst gives

[27]Aquilo and Horlenko, Formic Acid, *Hydrocarbon Process.* 59 (11) 120 (1980).

[28]Lowenheim and Moran, op. cit., p. 201.

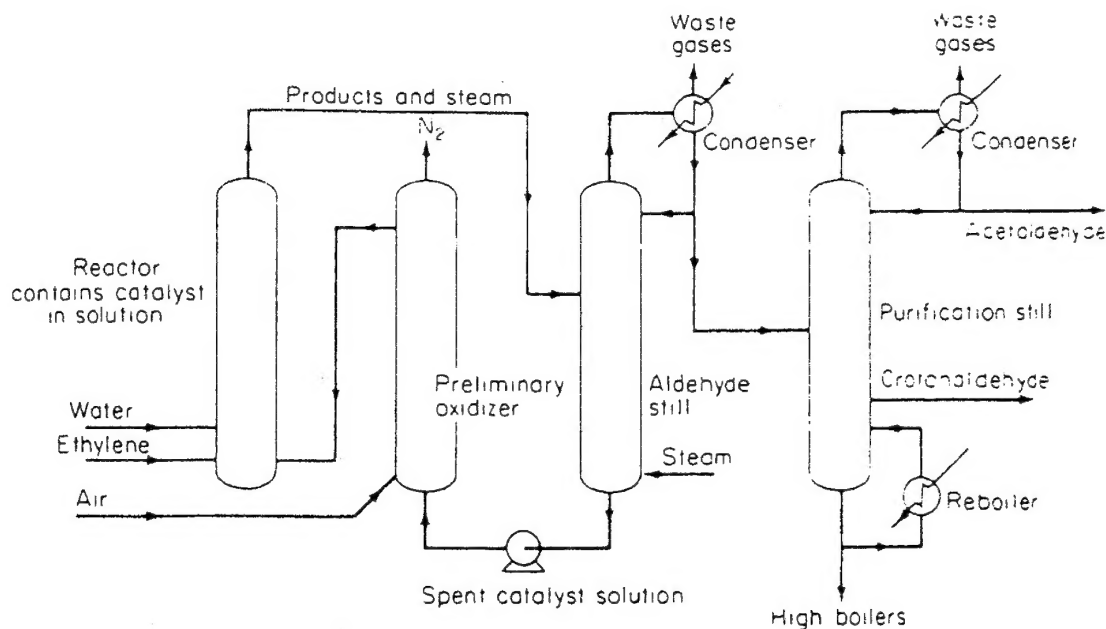[29]Acetaldehyde, *Hydrocarbon Process.* 60 (11) 121 (1981)
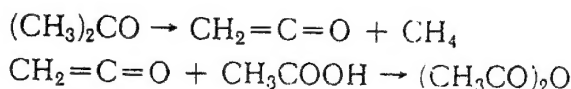

Fig. 38.9. Flowchart for acetaldehyde by air oxidation of ethylene.

about a 25 percent conversion to acetaldehyde, with recirculation making a 90 to 95 percent yield possible. (4) Lower molecular weight paraffin hydrocarbons are oxidized noncatalytically to produce mixed compounds, among them acetaldehyde and acetic acid. Separation of such mixtures is difficult.

Since nearly 50 percent of the acetaldehyde produced is used to make acetic acid, its future market is questionable. Acetic acid produced directly by the carbonylation of methanol[30] has already cut deeply into the market.
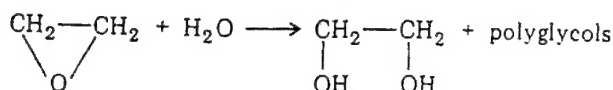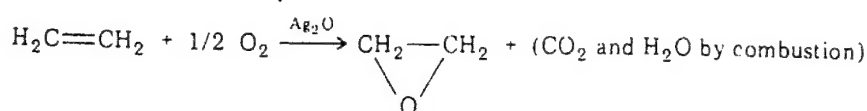
Acetic acid is widely used, and much is converted to acetic anhydride.[31]

Eastman[32] is currently building a very large plant to produce these and other chemicals from coal. The reaction between ketene and acetic acid produces the anhydride, but the amount of energy required to produce the ketene (acetone is cracked to give ketene and methane) is very large.

$$(CH_3)_2CO \rightarrow CH_2{=}C{=}O + CH_4$$
$$CH_2{=}C{=}O + CH_3COOH \rightarrow (CH_3CO)_2O$$

Ketene is used immediately after manufacture because it does not store well. The major use of acetic anhydride is in making vinyl acetate and other acetylations.

Ethylene glycol,[33] used in antifreeze, 40 percent, and in fibers and films, 50 percent, is a major petrochemical and has been for many years. The demand in 1981 was 2×10^9 kg. Like most of the other alcohols, it was originally made by reacting chlorine and water (HOCl) with ethylene to form the chlorohydrin, which was then hydrolyzed to yield glycol. This procedure and several others (formaldehyde + CO_2, fermentation, oxidation of propane) is now technically and environmentally obsolete. The currently favored process starts with ethylene and reacts it with oxygen or air in a tubular reactor over a silver oxide catalyst to form ethylene oxide. Because the volatility of glycol is low, it is preferable to purify the ethylene oxide, then convert it to glycol by hydration. During the hydration, however, polyglycols, particularly di- and tri-ethyleneglycols are formed. The reactions are:

$$H_2C{=}CH_2 + 1/2\ O_2 \xrightarrow{\ Ag_2O\ } CH_2{-}CH_2 \underset{O}{\diagdown\diagup} + (CO_2 \text{ and } H_2O \text{ by combustion})$$

$$CH_2{-}CH_2 \underset{O}{\diagdown\diagup} + H_2O \longrightarrow \underset{OH}{\overset{|}{C}H_2}{-}\underset{OH}{\overset{|}{C}H_2} + \text{polyglycols}$$

Ethylene dichloride (under 1 ppm) is added to a mix of ethylene and air in the ratio of $1{:}10$ to reduce oxidation to CO_2, and the mixture is passed over a supported silver oxide catalyst at atmospheric pressure and 280°C with a 1-s contact time. This causes a 60 to 70 percent

[30]Roth et al., Low Pressure Process for Acetic Acid via Carbonylation of Methanol, *CHEMTECH* 1 (10) 600 (1971).

[31]Jeffreys, *The Manufacture of Acetic Anydride*, 2d ed., The Institution of Chemical Engineers, London, 1964.

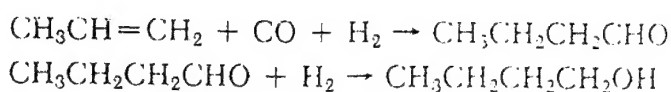[32]A Giant Step: Acetic Anhydride from Coal, *Chem. Week* 127 (3) 40 (1980).

[33]*Hydrocarbon Process.* 60 (11) 161–163 (1981).

conversion of the ethylene. Ethylene oxide is removed from the effluent by water scrubbing, and the unreacted constituents are recirculated.

Liquid-phase conversion of the ethylene oxide to glycol uses a dilute sulfuric acid solution at 60°C and is a quite slow reaction, requiring 30 min to 1 h. An excess of water is used, and the mono-, di- and triethylene glycols are separated by vacuum distillation.

Aromatic products by oxidation include the phthalic acids from xylenes or naphthalene (see Fig. 38.4 and Table 38.6), vanillin from eugenol (Chap 27), toluene to benzaldehyde and benzoic acid, cumene to cumene hydroperoxide, and benzene to maleic acid and anhydride. These have all been discussed elsewhere in this book.

HYDROFORMYLATION, THE OXO-REACTION. The oxo-reactions offer ways of converting α-olefins to aldehydes and/or alcohols containing an additional carbon atom. For example (Fig. 38.10):

$$CH_3CH=CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO$$
$$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$$

The olefin in a liquid state is reacted at 27 to 30 MPa and 150 to 170°C in the presence of a soluble cobalt catalyst. The aldehyde and a lesser amount of the alcohol are formed, flashed off along with steam, and the catalyst is recycled. Conversions of over 97 percent are obtained. The reaction is strongly exothermic. The CO and H_2 are usually in the form of synthesis gas. When propylene is used as the hydrocarbon, n- and iso-butyraldehyde are formed. This reaction is most frequently run with the C_3 and C_7 to C_{12} olefins. When C_7 olefins are used, a series of dimethyl- and ethylhexanols and methyl heptanols are formed which are used as "octyl" alcohols to make plasticizers and esters.
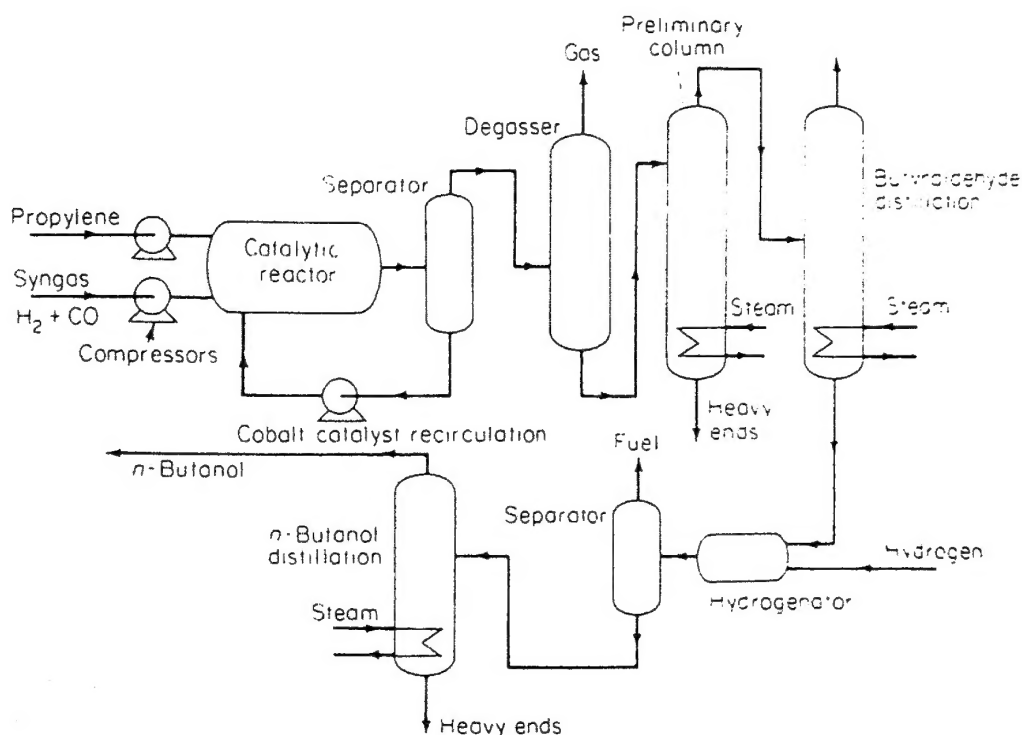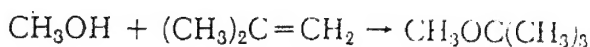

Fig. 38.10. Flowchart for butraldehyde and n-butanol by the oxo-synthesis

POLYMERIZATION. Polymerization has been covered already for a variety of processes. In Chap. 37, polymerization of low-molecular-weight hydrocarbons to form gasolines was examined. The reactions considered in Chaps. 34, 35, and 36 are mainly polymerizations.

MISCELLANEOUS. *Methyl tertiary butyl ether,* MTBE,[34] has excited considerable interest in recent years because it is a good octane enhancer for gasoline (it blends as if it had a research octane number of 115 to 135). It also offers a method of selectively removing isobutylene from a mixed C_4 stream, thus enabling the recovery of high-purity butene-1. Interest also arises because the MTBE can be isolated, then cracked to yield highly pure isobutylene and methanol. One plant uses this procedure to make pure tertiary butyl phenol (5×10^7 kg in 1981), and another is considering its use to make polyisobutylenes. The reaction for making MTBE proceeds quickly and highly selectively by reacting a mixed butene-butane fraction with CH_3OH in the liquid phase on a fixed bed of ion-exchange resin catalyst (Fig. 38.11). The reactions are:

$$CH_3OH + (CH_3)_2C=CH_2 \rightarrow CH_3OC(CH_3)_3$$

Reactor effluent is distilled, giving MTBE of 99% purity. A few percent of isobutylene remain unchanged and can be scavenged by use of a second unit.

Constantly increasing quantities of sulfur are recovered from refining operations and the processing of natural gas. Hydrodesulfurization frees sulfur, usually as H_2S, from the heavier fractions of petroleum, and this can be recovered. Frasch sulfur is more expensive than recovered sulfur, so it has become the material which supplies deficits of sulfur after the recovered sulfur is used up. This is precisely the condition in which acetone from isopropyl alcohol manufacturers find themselves. Sulfur is recovered by variants in the Claus process.

Carbon disulfide[35] is used principally for the manufacture of rayon. The traditional route[36] was by an electrothermal process using coal and sulfur, but most is now made by a catalyzed

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[34]Stinson, New Plants, Processes Set for Octane Booster. *Chem. Eng. News* **124** (26) 35 (1979); Taniguchi and Johnson, MTBE for Octane Improvement, *CHEMTECH* **9** (8) 502 (1979); *Hydrocarbon Process.* **61** (9) 177 (1982).

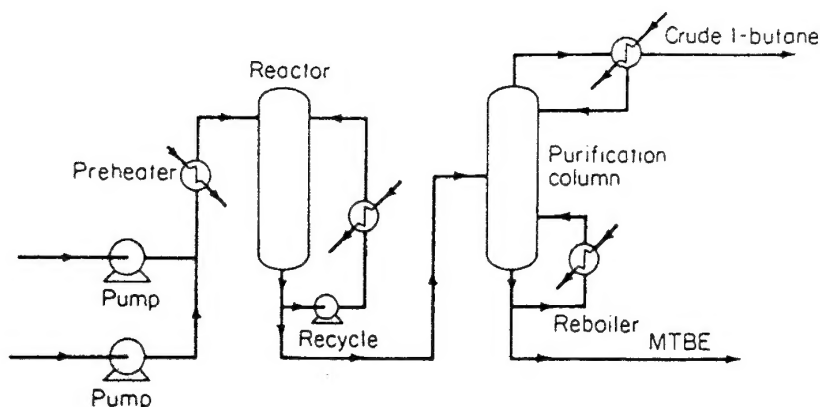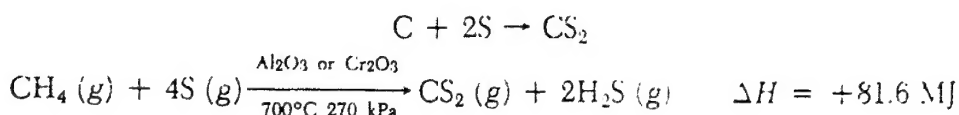[35]Haines, Carbon Disulfide, *Ind. Eng. Chem.* **55** (6) 44 (1963).

[36]See CPI 2, p. 336.

Fig. 38.11. Flowchart for methyl tertiary butyl ether (MTBE) and 1-butene manufacture.

reaction between methane and sulfur. The reactions are:

$$C + 2S \rightarrow CS_2$$

$$CH_4\,(g) + 4S\,(g) \xrightarrow[\text{700°C 270 kPa}]{\text{Al}_2\text{O}_3 \text{ or } \text{Cr}_2\text{O}_3} CS_2\,(g) + 2H_2S\,(g) \qquad \Delta H = +81.6 \text{ MJ}$$

The yield, based on methane, is around 90 percent per pass. The H_2S can be converted to sulfur and reused, or reacted with carbon to form more CS_2. Demand in 1980 was 171×10^6 kg.

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Chapter 6

Cyclic Intermediates and Dyes

HISTORICAL. Chemistry's first big breakthrough into the public eye came with the proliferation of quality dyestuffs replacing expensive, chronically short, and generally low-quality natural dyes. In those days, aromatic chemicals, usually in quite impure form, came exclusively from coal tar and neither their structure nor reactions were well understood. Sir William Henry Perkin discovered the first practical synthetic dye (mauve) while trying to synthesize quinine from aniline contaminated with toluidine. Since all dyes came from compounds derived from coal tar and most required the use of aniline, the synthetic dyes became known as coal-tar or aniline dyes. Sir Henry realized the importance of his discovery, patented it, and dominated the synthetic dye industry for seventeen years (1856 to 1873). He became quite rich in the process and retired at an early age to a life of scientific experimentation. Particularly after his retirement, the Germans and Swiss rapidly became leaders in the field and by 1914 the Germans made 87 percent of the world's dyes. World War I cut off the supply of German dyes, and this led the United States to establish a domestic industry. The dye industry has always been highly competitive, and the United States has recently lost a significant percentage of its domestic market to Swiss, German, Japanese, and Italian competition. There are several major American companies that have dropped dye manufacture since 1978.

ECONOMICS AND USES. Dyes generally have rather complicated structures which are made by reactions involving building blocks known as intermediates. Most of these are aromatic compounds with substituent groups such as $-NH_2$, $-OH$, $-NO_2$, and $-SO_3H$ which alter the reactivity of the cyclic compound and sometimes the color of the dye. Intermediates are not used just for the manufacture of dyes, but for all types of organic work where complex structures are built up. They are particularly useful for making agricultural chemicals, pesticides, pharmaceuticals, and rubber chemicals. Table 39.1 shows the size of the markets involved. This specialized business produces around 2000 compounds, most at rates of 0.5 to 1.5×10^6 kg/year. Most intermediates sell for around $1.00 per kilogram. These substituted aryl compounds are usually made from benzene, toluene, or naphthalene, and their price goes up as the number and complexity of the substituents increase. Many are made by batch processes, and good chemistry is required to assure preparation of the isomer desired. Where a 1,4-substitution is desired, the 1,2- and 1,3-substituted material may be of value only as a fuel. Making these unwanted materials, however, comsumes valuable raw material to form potential (often actual) polluters.

There is an astonishingly large literature concerning reactions of aromatic compounds, much of it going back to the nineteenth century. Some of the information is still highly useful and valuable today.

Table 39.1 Synthetic Organic Chemicals and Their Raw Materials: U.S. Production and Sales

| | Production, 10^6 kg | | Sales | | | |
| | | | Quality, 10^6 kg | | Value, 10^6 \$ | |
	1972	1980	1972	1980	1972	1980
Tar	3,396	1,970	1,549	1,422	40	n.a.*
Tar crudes	3,608	n.a.	2,411	n.a.	126	n.a.
Crude products from petroleum and natural gas	39,451	54,651	21,773	29,224	1,177	10,645
Synthetic Organic Chemicals						
Cyclic intermediates	15,894	20,486	7,362	9,118	1,434	7,248
Dyes	120	111	116	103	480	791
Synthetic organic pigments	30	32	24	28	149	361
Medicinal chemicals	106	111	74	76	490	1,153
Flavor and perfume materials	50	80	47	59	88	254
Plastic and resin materials	11,782	17,357	10,430	15,250	4,258	16,011
Rubber processing materials	164	132	127	88	178	296
Elastomers	2,234	2,168	1,880	1,481	1,095	2,280
Plasticizers	1,836	811	1,026	715	451	858
Surface-active agents	n.a.	2,206	n.a.	1,354	n.a.	1,296
Pesticides and other agricultural products	526	667	465	639	1,092	4,078
Miscellaneous chemicals	41,125	53,623	20,525	22,825	4,680	15,171
Grand total	120,322	154,405	67,809	82,382	15,738	n.a.

*n.a., not available

The whole procedure of intermediate manufacture is generally labor intensive, which makes it difficult for United States companies to compete. The recent emphasis on identification and control of toxicants has provided additional harassment. Determining the toxicity of materials that are made in such small quantities may well cost more than years of potential profit.

RAW MATERIALS. Both inorganic and organic materials are needed to make dyes and intermediates, but the backbone of the raw-material sequence is:

Petroleum→aromatic hydrocarbons→intermediates→dyes

Aromatic hydrocarbons were once scarce, at least in the high purities desired for making cyclic intermediates, because of the scarcity of coal tar and the difficulty in separating it into pure materials. The abundance of raw materials now available from petroleum is not an unmixed blessing, for there is fierce competition for many fractions which are desired by other users. At the same time, there remain interesting aromatic fractions of coal tar for which uses have never been developed and which are simply burned.

The demands of the dye industry for raw materials from which to make intermediates, or precursors of intermediates, played a major part in bringing about the change from beehive to by-product coke ovens. The source of the major hydrocarbons desired for making intermediates, e.g., benzene, toluene, naphthalene, anthracene, xylene, and some paraffins and

olefins, is now the special aromatized naphthas resulting from the catalytic refining of selected petroleum crudes. Under 1 percent are coal-derived.

For some complicated intermediates, the use of inorganic acids, bases, and halogens in manufacture is surprisingly high. There are anthraquinone dyes that require over 75 kg of chemicals to produce 1 kg of dye.

INTERMEDIATES

A few intermediates are made in very large quantities and enjoy their principal use outside the field of dyes. Many, originally extracted from coal tar, are now made synthetically. See Table 39.2. The following intermediates were made in quantities in excess of 400×10^6 kg in 1980 (note that most of these have already been covered in other chapters): ethyl benzene, dimethylterephthalate, p-xylene, cumene, and phenol. Isocyanates, o-xylene, alkyl benzenes, phthalic anhydride, cyclohexanone, aniline, nitrobenzene, bisphenol A, monochlorobenzene, and toluene-2,4-diamine were produced on a lesser, but still very large scale. These two sets account for nearly 90 percent of the total output of intermediates, but this chapter is concerned primarily with the other 10 percent.

The census of intermediates taken by the U.S. International Trade Commission shows that in 1980 the United States produced 2.05×10^{10} kg of cyclic intermediates, a 9 percent decline from the previous year, caused primarily by the general decline in business. These materials were valued at $7.27 million.

Table 39.2 Production of Important Cyclic Intermediates (in thousands of kilograms

	1972	1980
Acetanilide, technical	1,474	4,357
Aniline	186,282	299,737
Benzoic acid, technical	70,684	33,370
Chlorobenzene, mono	183,411	128,560
Cresols, total	48,306	47,927
Cresylic acid, refined, total	24,991	17,395
Cumene	1,042,273	1,572,273
Cyclohexane	1,044,545	892,727
Cyclohexanone	356,109	348,552
o-Dichlorobenzene	28,357	22,175
p-Dichlorobenzene	35,144	34,115
Ethylbenzene	2,580,000	3.473,640
4,4'-Isopropylidenediphenol (bisphenol A)	115,995	240,767
α-Methylstyrene	16,999	17,612
Nitrobenzene	250,531	278,012
5-Nitro-o-toluenesulfonic acid	3,644	
Nonylphenol	45,589	66,927
o-Xylene	378,083	452,239
p-Xylene	1,003,636	1,926,363
Phenol	952,784	1,167,045
Phthalic anhydride	433,172	371,930
Salicylic acid, technical, sales	21,407	17,750
Styrene	2,700,454	3,116,360

Unit Operations

No operations are used in intermediates manufacture that have not been described in previous chapters, particularly Chap. 38.
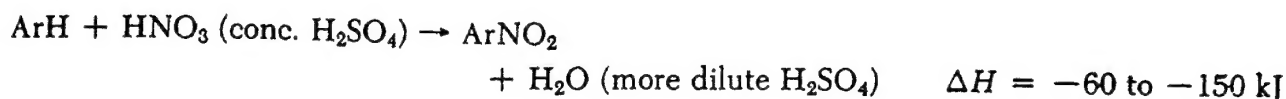
Chemical Conversions

The chemical conversions of this chapter are mainly concerned with aryl substances; those of Chap. 38 with aliphatic and naphthenic substances, but the conversions involved and the general approaches to manufacture are strikingly similar. In manufacturing petrochemicals, the focus was not so much on the effect of the substitution on subsequent reactions as it is for cyclic intermediates, but the reactions are similar.

ISOMERS. With benzene, monosubstitution produces a single substance, but with naphthalene and anthraquinone, there are two possible monosubstitutions. With polysubstitution, the possibilities for isomers become quite large. The ability to react to form the substance desired, or to yield the color or physiological reaction wanted, depends on creating the correct isomer, largely to the exclusion of all others. Here chemical skill is of the utmost importance, for some substituents encourage ortho and para substitution, others encourage meta. Rules for substitution, the early ones based upon observation and surmise and later ones based on physical chemical theory, are covered in detail in several works on intermediate synthesis.[1] Substituents are important beyond their contribution to molecular geometry in that they can alter the solubility of the molecule in acid or basic solvents and possess directional effects on ensuing nucleophilic substitutions.

NITRATION. Before the ability to work with and control high pressures became commonplace, thus enabling ammonolysis to be run readily, the standard way to put an amino group on an aryl nucleus was by nitration, then reducing the aryl nitro compound to an amine. The amino-substituted compound could then be subjected to the diazotation reaction by treating it with $NaNO_2$ in cold solution. This reactive material could then be coupled with another compound to give the azo configuration, the major chemical group for many dyes. Very few nitro groups appear in finished dyes. Most have been reduced to the more reactive amine in the course of dye formation.
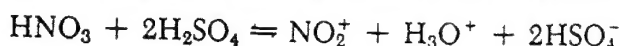
A typical nitration reaction is:

$$ArH + HNO_3 \text{ (conc. } H_2SO_4) \rightarrow ArNO_2$$
$$+ H_2O \text{ (more dilute } H_2SO_4) \qquad \Delta H = -60 \text{ to } -150 \text{ kJ}$$

The presence of sulfuric acid in quantity is vital to the success of the nitration because: (1) it reduces the ionization $HNO_3 \rightleftharpoons H^+ + NO_3^-$ which increases as the water-producing reaction dilutes the reaction mixture. Additional strongly oxidizing NO_3^- ions cause destruction of the organic reactants and products. (2) It acts as an energy reservoir to prevent destructive rapid temperature rise and provides a vehicle to convey heat to the jacket and/or coil. (3) It
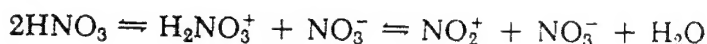
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[1]ECT, 3d ed., vol. 8, 1979, p. 159 ff; Rys and Zollinger, *Fundamentals of the Chemistry and Application of Dyes*, Wiley-Interscience, New York, 1972; Fierz-David and Blangey, *Fundamental Processes of Dye Chemistry*, Interscience, New York, 1949.

increases the solubility of the hydrocarbon in the reaction mix, thus speeding up the reaction. (4) It promotes the ionization of the nitric acid to give NO_2^+, the nitronium ion, which is the nitrating species. The nitronium ion is formed as follows.

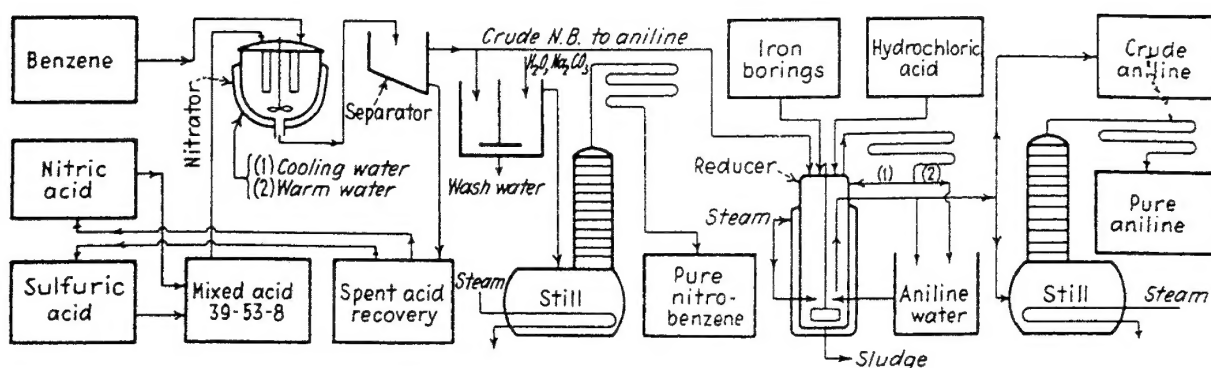### In Mixed Nitric-Sulfuric Acid (Commonly Called Mixed Acid)

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

In Nitric Acid

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Absorption of water by sulfuric acid favors the nitration reaction and shifts the equilibrium to the right. Considerable heat evolution accompanies the nitration reaction, oxidation increases it, and the heat of dilution of the sulfuric acid increases it still farther. Increased temperature favors dinitration and oxidation so the reaction must be cooled to keep it under control. Good heat transfer can be assured by the use of jackets, coils, and good agitation in the nitrator. Nitrators are usually made of stainless steel, although cast iron stands up well against mixed acid. Figure 39.1 gives some data for nitrobenzene manufacture. Lists of important nitrations along with notes concerning the raw materials used and some details of manufacture are available.[2]

Most commercial nitrations are made with mixed acid, but there are other useful nitrating

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[2] CPI 4, p. 717; Abrahart, *Dyes and Their Intermediates*, Pergamon, Oxford, 1977; Groggins, *Unit Processes in Organic Syntheses*, McGraw-Hill, New York, 1958.

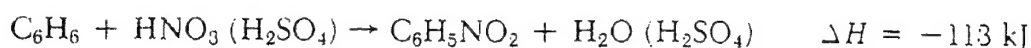The following materials and utilities are required to produce:

NITROBENZENE, 1 t

Benzene	655 kg	Sodium carbonate	10 kg
HNO_3	530 kg	Power (% of total cost)	3.2
H_2SO_4	721 kg	Labor (% of total cost)	2.4
H_2O	109 kg	Overhead (% of total cost)	8.3

ANILINE, 1 t

Nitrobenzene	1390 kg	Power (% of total cost)	6.4
Iron borings	1600 kg	Labor (% of total cost)	8.0
HCl (30%)*	125 kg	Overhead (% of total cost)	4.0

*Or an equivalent amount of aniline salt mother liquor.

Fig. 39.1. Flowchart for production of nitrobenzene and aniline by reduction.

agents, e.g., inorganic nitrates, oxides of nitrogen, nitric acid + acetic anhydride, and nitric + phosphoric acid.

Example of a Technical Nitration. Nitrobenzene from benzene is used mainly for reduction to aniline, where it must compete with aniline by ammonolysis.

$$C_6H_6 + HNO_3 \ (H_2SO_4) \rightarrow C_6H_5NO_2 + H_2O \ (H_2SO_4) \qquad \Delta H = -113 \ kJ$$

Plants are simple with large (3000 to 5000 L) nitrators operating batchwise or small continuous (Biazzi or similar) units. The temperature is held at about 50°C, governed by the rate of feed of benzene. Reaction is quite rapid (15 to 20 min) in well-stirred and continuous nitrators. The reaction products are decanted from the spent acid and are washed with dilute alkali. The spent acid is sent to some type of recovery system. Yields of 98 percent of theory are common.

SULFONATION. Since sulfuric acid is comparatively cheap, it is desirable to use it for nucleophilic substitution wherever possible. The fundamental chemistry has been well studied[3] and a list of important sulfonations is available.[4]

The reaction may be expressed as:

$$ArH + (HO)_2SO_2 \rightarrow ArSO_2OH + H_2O$$

The usual sulfonating agent is concentrated sulfuric acid, but SO_3, chlorosulfonic acid, metallic sulfates, and sulfamic acid are also occasionally used. For each substance being sulfonated, there is a critical concentration of acid below which sulfonation ceases. The removal of the water formed in the reaction is therefore essential. The use of a very large excess of acid, while expensive, can maintain an essentially constant concentration as the reaction progresses. It is not easy to volatilize water from concentrated solutions of sulfuric acid, but azeotropic distillation can sometimes help. Sulfonations are exothermic, but not highly corrosive, so they can be conducted in steel, stainless-steel, or cast-iron sulfonators. A jacket heated with hot oil, Dowtherm, or steam can serve to heat the contents sufficiently to get the reaction started, then carry away the heat of reaction. A good agitator, a condenser, and a fume control system are usually also provided.

Example of a Technical Sulfonation. 1- and 2-Naphthalene sulfonic acids are formed simultaneously when naphthalene is sulfonated with concentrated sulfuric acid. The isomers must be separated if pure α- or β-naphthol are to be prepared from them, and this offers some difficulty. Variations in time, temperature, sulfuric acid concentration, and acid/hydrocarbon ratio alter the yields to favor one particular isomer, but a pure single substance is never formed. Using similar acid/hydrocarbon ratios, sulfonation at 40°C yields 96% alpha isomer, 4% beta, while at 160°C the proportions are 15% alpha, 85% beta.

The α-sulfonic acid can be hydrolyzed to naphthalene[5] by passing steam at 160°C into the

[3]Venkataraman, *The Chemistry of Synthetic Dyes*, several volumes, Academic, New York, 1952–1974; Groggins, op. cit., p. 303.

[4]CPI 3, p. 723.

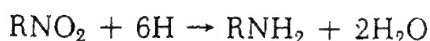[5]Shreve, beta-Naphthol, *Color Trade J.* 14, 42 (1924); Groggins, op. cit., p. 316.

sulfonation mass. The naphthalene so formed passes out with the steam and can be recovered. The pure beta acid left behind can be hydrolyzed by cautic fusion to yield relatively pure β-naphthol.

Isolation of a specific isomer is rarely this simple. Separations are based on some of the following consideration:

1. Variations in the *rate* of hydrolysis of two isomers (as above).
2. Variations in the solubility of various salts in water.
3. Differences in solubility in solvents other than water.
4. Differences in solubility accentuated by common-ion effect (salt additions).
5. Differences in properties of derivatives.
6. Differences based on molecular size, such as using molecular sieves or absorption.

The fourth edition of CPI[6] gives an extensive list of commercial sulfonations.

AMINATION BY REDUCTION. Color in dyes frequently results from conjugated systems involving nitrogen and these are formed from amino groups. For years, the only method of putting an amino group on an aryl nucleus involved adding an $-NO_2$ group, then reducing. Without high-pressure vessels and modern catalysts, reduction had to be done by reagents which would function under atmospheric pressure. The common reducing agents available under these restrictions are: (1) iron and acid, (2) zinc and alkali, (3) sodium sulfide or polysulfide, (4) sodium hydrosulfite, (5) electrolytic hydrogen, and (6) metal hydrides. Now liquid and gas phase hydrogenations can be performed on a variety of materials. The typical reaction is:

$$RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$$

The energy given off by this type of reaction is quite large.

Where metals are used to produce the reducing hydrogen, several difficult processing problems are created. The expense is so great that it is necessary to find some use for the reacted material. Spent iron can sometimes be used for pigment preparations or to absorb H_2S. Stirring a vessel containing much metal is quite difficult.

On a small scale, hydrogen for reduction can be produced by cracking ammonia. Transport and storage of hydrogen as ammonia is compact, and the cracking procedure involves only a hot pipe packed with catalyst and immersed in a molten salt bath. The nitrogen that accompanies the generated hydrogen is inert.

Example of a Technical Amination by Reduction. Aniline Production. In 1982, 3.09 $\times 10^8$ kg of aniline were produced, 55 percent of which were used to make p,p'-methylene diisocyanate, 20 percent went into rubber chemicals, and only 10 percent into intermediates and dyes. Most was made by catalytic reduction of nitrobenzene with hydrogen, which is practiced as shown in Figs. 39.2 and 39.3.

AMINATION BY AMMONOLYSIS. The replacement of a nuclear substituent such as $-OH$, $-Cl$, or $-SO_3H$ with $-NH_2$ by the use of ammonia has been practiced for some time with molecules having labilizing substituents (groups nearby making replacement easier). For example, 1,4-dichloro-2-nitrobenzene can be changed readily to 4-chloro-2-nitroaniline by
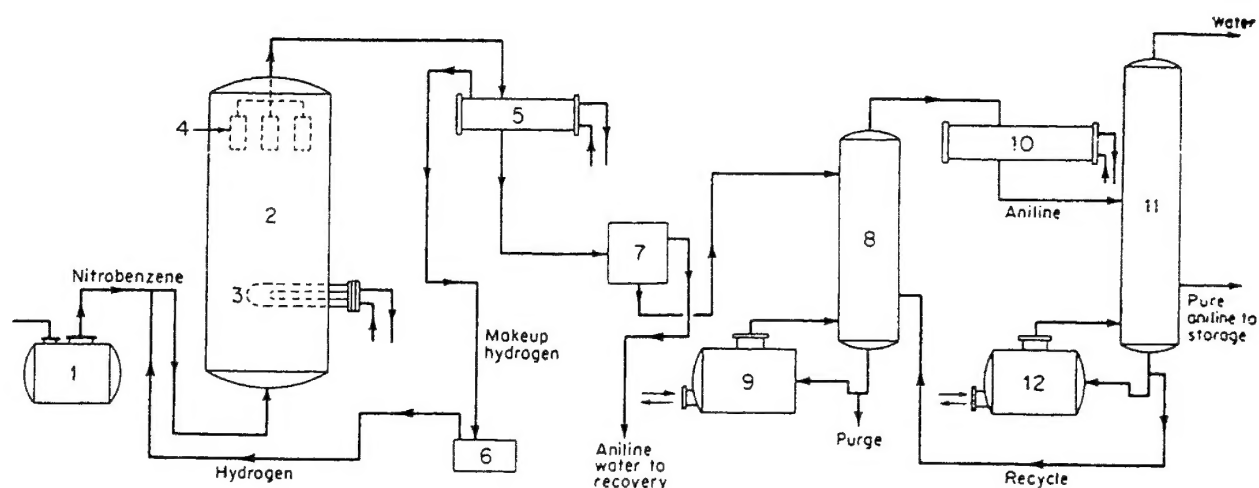
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[6]CPI 4, p. 724.

Fig. 39.2. Continuous fluid-bed vapor-phase reduction of nitrobenzene. (1) Nitrobenzene vaporizer, (2) reactor with fluidized catalyst bed, (3) cooling tubes, (4) catalyst filters, (5) product condenser, (6) hydrogen recycle compressor, (7) aniline water settler and decanter, (8) crude aniline still, (9) reboiler for crude aniline still, (10) condenser, (11) aniline finishing still, (12) reboiler for aniline finishing still. *(American Cyanamid Co.)*
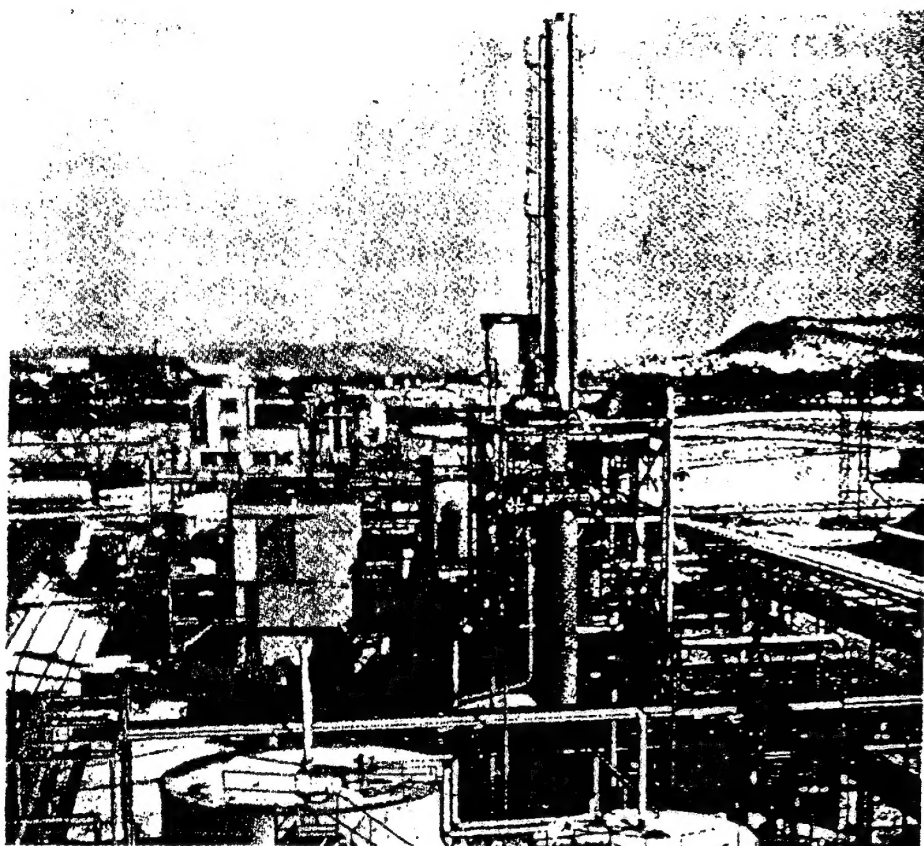

Fig. 39.3. Overall view of the vapor-phase aniline manufacturing facilities at Willow Island, W. Va. *(American Cyanamid Co.)*

treatment with aqueous ammonia. Other molecules offer more processing difficulty, and pressure vessels are required for the production of aniline[7] from chlorobenzene or phenol

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

Ammonia is a comparatively low-cost reagent. The other routes to amines through reduction use expensive reagents (Fe, Zn, or H_2 gas) that make ammonolysis costs quite attractive. Substituted amines can be produced by using substituted ammonia (amines) in place of simple ammonia.

Equipment is some type of agitated pressure vessel made entirely of iron; stainless steel is rarely necessary. Figure 39.4 shows a flowchart for the manufacture of aniline from phenol.[7] Lists of intermediates made by ammonolysis and the conditions involved are available.[8]

HALOGENATION.[9] Halogenation is almost always chlorination, for the difference in cost between chlorine and the other halogens, particularly on a molal basis, is quite substantial. In a very few cases, Br, I, or F confer properties special enough to warrant the additional expense, but large-scale operations are not based on them. Chlorine and hydrochloric acid are used to cause substitution (and occasionally addition) on aryl ring compounds. Chlorination proceeds (1) by addition to an unsaturated bond, (2) by substitution for hydrogen, or (3)

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[7]McKechnie, Bayer, and Drennan, Aniline: Phenol Feed Chosen, *Chem. Eng.* 87 (26) 26 (1980). Polinski and Harvey, Aniline Production by Dual Function Catalyst, *Ind. Eng. Chem., Prod. Res. Develop.* 10 (4) 365 (1971).

[8]Groggins, op. cit., chap. 8; CPI 4, p. 721.
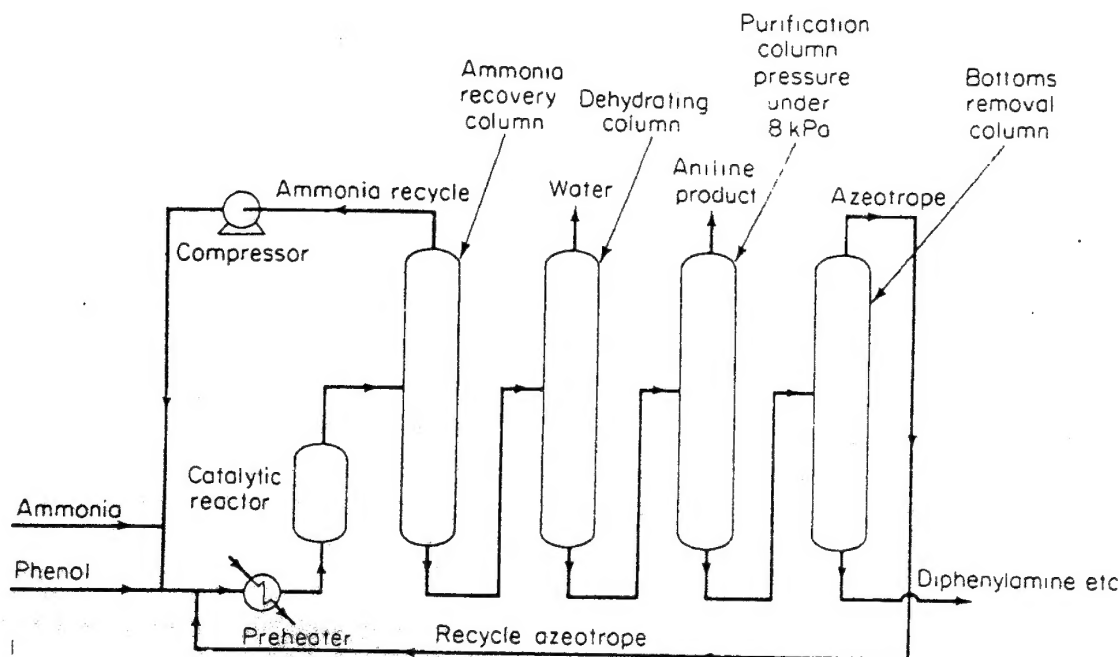
[9]Groggins, op. cit., chap. 6.

Fig. 39.4. Flowchart for aniline from phenol.